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Investigation of the Kinetics of Crystallization of Molten Binary and Ternary Oxide Systems

Quarterly Status Report No. 1 - September 1, 1965 through November 30, 1965

Contract No. NASW-1301

SUMMARY

This report summarizes the progress made in the first quarter of the experimental research investigation of the kinetics of crystallization of molten binary and ternary oxide systems. During this quarter, the first oxide system selected for investigation ($Mg_2Al_4Si_5O_{18}$) was successfully melted and electrical conductivity measurements obtained from 860 C to 1560 C. Young's modulus measured for the bulk glass was 15 x 10^6 pounds per square inch.

This investigation is being carried out under Contract NASW-1301 with the Materials Research Branch.

INTRODUCTION

This is the first quarterly status report for Contract NASW-1301 entitled "Investigation of the Kinetics of Crystallization of Molten Binary and Ternary Oxide Systems" covering the period September 1, 1965 through November 30, 1965. In this study the kinetics of crystallization are being investigated for three oxide systems both with and without anti-nucleating agents by measuring the electrical conductivity, viscosity, and surface tension of the molten oxide system. The three oxide systems will be selected from systems which tend to form complex three-dimensional structures. Ultimately, the objective of this program is to form glass fibers of high strength and high modulus from glasses not customarily deemed suitable for this purpose.

DISCUSSION

Progress has been made in several areas in the first three months of the contract period. Reports from programs previously sponsored by the Government in the area of glass fiber research together with the published literature in this field appearing in the last ten years have been reviewed. Examination of the many Government-sponsored research contracts in this area (Refs. 1 through 39) has shown that although several thousand glass compositions have been melted in an effort to produce improved glass fibers no conflict exists with the directions of research planned by UACRL. Only one other contractor, Refs. 14 through 17, has been concerned with structured glasses and this contractor has largely concentrated on patterning glasses after those materials exhibiting an infinite linear chain structure such as asbestos, the pyroxenes, the amphiboles, the diopsides, and the spodumenes. The hope of this research was that by forming glass fibers from glass melts which have linearly orientable groupings of atoms, this orientation would persist in the molten state and would, therefore, yield an oriented or anisotropic glass fiber of high strength and modulus. It can be seen, accordingly, that the theoretical considerations motivating these investigators as well as their choice of structures to be investigated (Refs. 14 through 17) are distinct when compared to the current investigation. However, toward the end of the first contractual period these investigators did include the cordierite glass field composition as the only ring-type silicate structure (glass composition C-7, pg. 45, Ref. 16) investigated and found it to be difficultly fiberizable (pg. 46) but did not otherwise characterize it because of time limitations (pg. 51). No mention is made (Refs. 14 through 17) of the other ring-type silicate structures proposed for study in the current investigation.

The first oxide system to be selected for investigation, cordierite or $Mg_2Al_4Si_5O_{18}$ - a three-dimensional ring former, has been melted successfully repeatedly in several atmospheres and in several containers. Equipment developed for monitoring the electrical conductivity of the molten oxide system as it cools has been used successfully to measure the electrical conductivity of the vitreous cordierite system from 1560 C to 860 C. Apparatus put together to carry out the dynamic measurement of Young's Modulus of the bulk glass has consistently yielded a result for glasses in the cordierite composition field of 15×10^6 pounds per square inch or 10.55 kilograms per square centimeter. Initial experiments on the second oxide system selected for study, benitoite or $BaTiSi_3O_9$ - a cyclic silicon oxygen complex having discrete $Si_3O_9^{6-}$ ions, have shown that this system devitrifies much more readily than the cordierite system.

Glasses in the cordierite glass field starting with 5 micron particle size high purity silica, alumina of 325 mesh size and 99% purity, and laboratory reagent grade magnesium carbonate as raw materials have been successfully melted. These materials yield a water-white optical grade glass free of seed, stone, and bubbles when held at a temperature of 1540 C or higher for a period of at least two hours. The glass may either be prepared in the highest purity commercially available fully recrystallized alumina crucibles in air at temperatures of 1520 C to 1540 C or in tungsten crucibles in either argon or vacuum atmospheres at temperatures of 1540 C and higher. Alumina crucibles of even slightly lower purity, i.e. 99.3% cf. to 99.7%, cannot be used nor can the temperature of 1540 to 1560 C be exceeded even with the highest purity alumina crucible.

To study the electrical conductivity of the cordierite based glasses as a function of time and temperature, the glasses were melted as described above and then broken up and packed into the tungsten crucible shown in Fig. 1. This crucible, which is pictured at the conclusion of the measurement, is made to serve as a conductivity cell by introducing a tungsten ball, one-quarter inch in diameter, on the end of a tungsten rod into the exact center of the crucible and by tying a tungsten rod to the outside of the crucible with 25 mil tantalum wire. The whole assembly is then placed in the tungsten resistance furnace shown in Fig. 2 and heated until the glass is completely remelted. Power to the furnace is then turned off and the electrical conductivity of the molten oxide system is measured continuously through the solidification process as the furnace cools. The temperature of the crucible is measured at thirty-second intervals to obtain the required data connecting electrical conductivity with crystallization or lack of crystallization rates.

The actual measurement of the electrical conductivity is carried out by connecting externally the UACRL "log ohmmeter" described schematically in Fig. 3 to the two leads from the tungsten crucible conductivity cell. These leads are brought out of the furnace using vacuum-type electrical lead-ins. The log ohmmeter of Fig. 3 is designed to measure resistance from 10^{-1} ohms to 10^{+6} ohms and generates a d-c signal voltage proportional to the logarithm of the resistance. The scale for this instrument is divided into six ranges: 10^{+6} ohms to 10^{+5} ohms, 10^{+5} to 10^{+3} ohms, 10^{+3} to 10^{+2} ohms, 10^{+2} ohms to 10 ohms, 10 ohms to 1 ohm, and 1 ohm to 10^{-1} ohm. Over each range, the amplitude of the signal applied to the unknown resistor and the sampling resistor are adjusted so that the power dissipated in the sample is less than 500 microwatts, and the sample resistor is less than 6.5 percent of the resistance being measured.

In each range position, a constant amplitude, 1000 cycle/sec, sinusoidal voltage is applied to the unknown and the current through it measured by a sampling resistor. This signal is passed through a series of filters consisting of a band-pass filter from 800 to 2000 cycles/sec, a twin-tee notch filter at 60 cycles/sec and a twin-tee notch filter at 180 cycles/sec in cascade. These filters effectively remove the large amount of noise generated in the sample by the massive (1000's of amperes) 60 cycle heater current present in the tungsten furnace. The signal is then linearly amplified by a guarded amplifier to a level of 0.5 volts p-p to 50 volts p-p and used to drive a power amplifier. The power amplifier isolates the guarded amplifier from the detector. The d-c voltage from the detector is then applied to the logarithmic converter which puts out a d-c voltage proportional to the logarithm of the input voltage. A unity gain operational amplifier following the logarithmic converter provides the low output impedance necessary to drive the strip chart recorder.

Besides the glass melting experiments and the monitoring of the electrical conductivity of these glasses by the equipment built and assembled for this purpose, apparatus was also set up for measuring Young's Modulus on bulk glass specimens by sonic (dynamic) circuitry. A rectangular or cylindrical beam in flexure vibrates at a resonant frequency determined by the dimensions, density and Young's Modulus of the specimen. If shear and inertia effects are considered, the formula for rectangular specimens is

$$E = \frac{(9.65)(10^{-7})ML^3f^2}{a^3b} \left[1 + 7.4 \left(\frac{a}{L} \right)^2 \right] \longrightarrow \text{kilograms/cm}^2$$

where M = mass of sample in grams
a = thickness of sample in inches
L = length of sample in inches
b = width of sample in centimeters
f = resonant frequency of sample in cycles/sec
E = Young's Modulus for sample in kilograms per square cm.

The equipment used to carry out the measurement is shown in Fig. 4. The specimen is placed on two narrow supports fashioned from sponge rubber, a highly absorbing material. A microphone supplied by a variable frequency oscillator is placed below the center of the specimen. This microphone excites the short column of air between itself and the specimen and this column of air in turn drives the specimen. At a given critical frequency the specimen resonates and this motion is detected by a phonographic pickup cartridge which touches the specimen directly over one of the supports. The signal from the phonographic pickup is then fed through an amplifier to one set of plates of an oscilloscope. The other set of plates of the oscilloscope is supplied from the oscillator output so that at the resonant frequency a Lissajous figure of maximum dimension is seen on the oscilloscope because of the 90^{o} phase shift occurring during detection. At any frequency other than the resonant frequency only a simple horizontal trace forms on the oscilloscope screen so that resonance is readily detectable. The circuitry shown in Fig. 4 when applied to six different specimens of the cordierite based glass yield the data given in Table I below.

Table I. Dynamic Modulus for Cordierite Based Glasses

Specimen	Mass gms	Dimensions a (in.)	b (cm)	L (in.)	Young's Modulus Kg/cm^2 x 10^5	pounds/in.^{2} x 10^6
Batch 4 - #1	1.2242	0.125	0.320	1.796	10.35	14.8
Batch 4 - #2	1.3698	0.1255	0.319	2.023	10.59	15.1
Batch 4 - #3	1.2508	0.126	0.320	1.850	10.55	15.0
Batch 14 - #1	1.70083	0.1273	0.324	2.406	10.52	15.0
Batch 14 - #2	1.5334	0.1275	0.324	2.173	10.55	15.0
Batch 14 - #3	1.4098	0.1277	0.324	2.025	10.74	15.0

The results obtained are interesting since using the same apparatus values for Corning Glass Works glasses Code 7940 (fused silica) of 10.5 x 10^6, Code 7740 (Pyrex) of 9.3 x 10^6, and Code 7052 (alumina-silica) of 8.2 x 10^6 pounds per square inch were obtained. The results obtained are also highly concordant.

The final item on which progress was made during this quarter consisted in selecting the second glass field to be investigated and preliminary trials at obtaining optical grade glass from the batches selected. The composition area selected is that of benitoite, $BaTiSi_3O_9$, whose structure is much like that of beryl (emerald), $Be_3Al_2Si_6O_{18}$, and is comprised of ring ions arranged in sheets with their planes parallel but not a layer structure since the metal ions lie between the sheets and bind together the rings of the different sheets. Preliminary experiments in melting this composition showed that it could not be contained in high purity alumina, magnesia, or beryllia and that when melted in platinum, the melt completely devitrified presumably because of nucleation by contact with platinum.

In the next quarter the search will be continued for a suitable container for melting benitoite based glasses and a study will be made of the effects of nucleating and anti-nucleating agents using both the cordierite and benitoite batches. The electrical conductivity will be measured in each case and the equipment now at hand for measuring viscosity by the restrained sphere method will be tested and used for both types of glass systems. Additional elastic moduli measurements will be made.

Personnel active on this program during this period were J. F. Bacon, principal investigator and Norman J. Chamberlain, Senior Experimental Technician. They were aided repeatedly throughout the period by Louis J. Tempel, Jr. of the UACRL Instrumentation Section.

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TUNGSTEN CRUCIBLE CONDUCTIVITY CELL

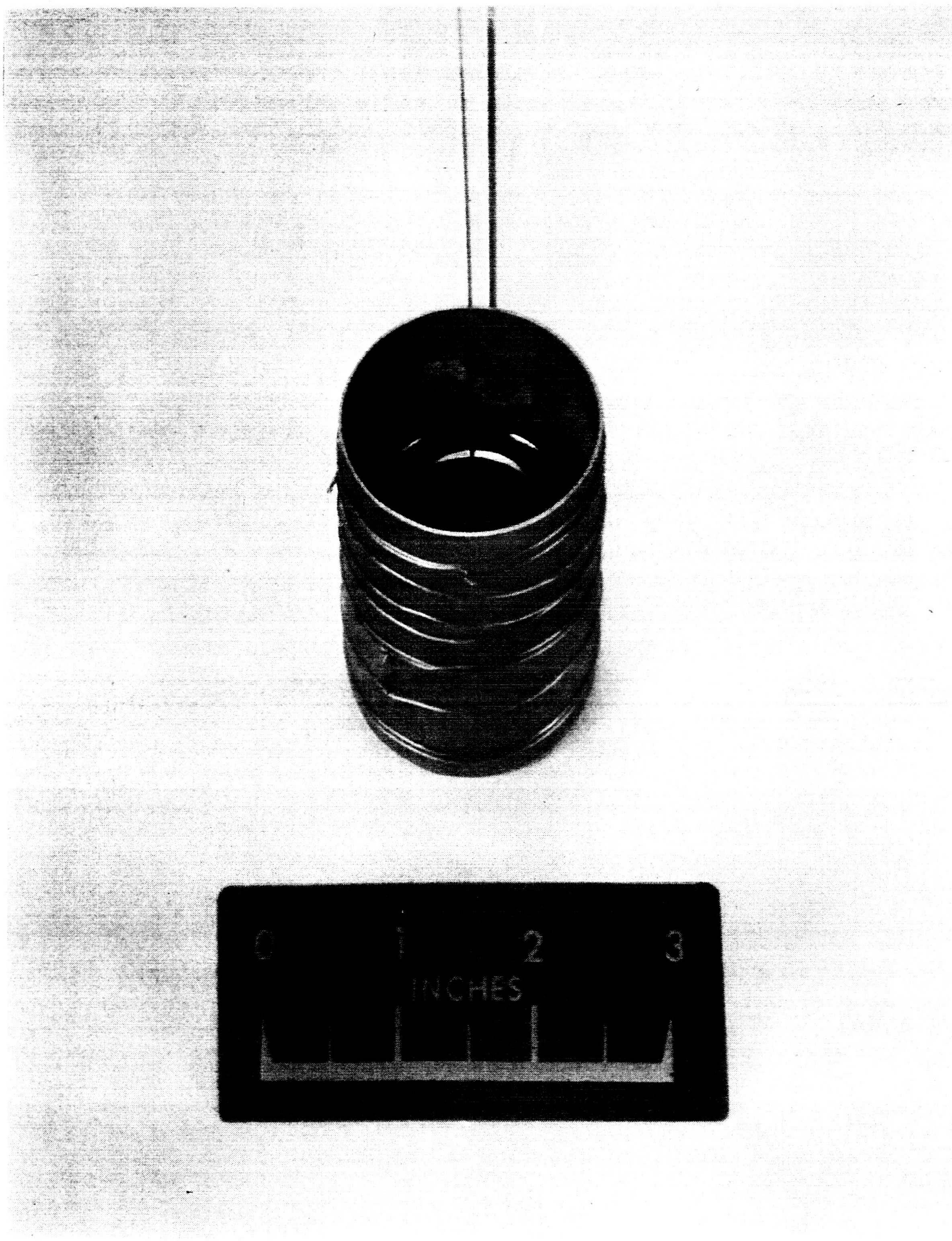

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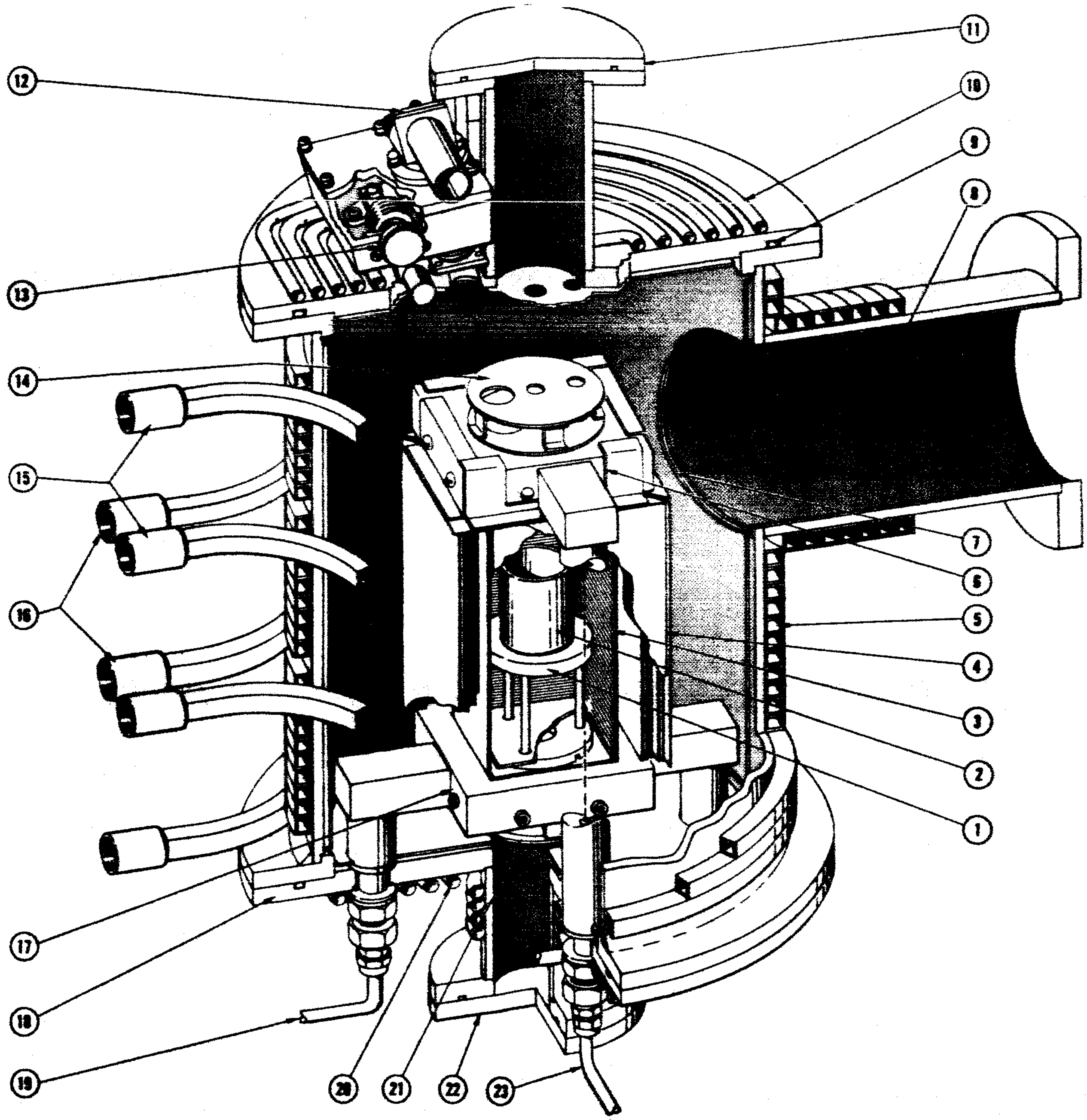
FIG. 2

TUNGSTEN RESISTANCE FURNACE



1. TUNGSTEN PEDESTAL FOR CRUCIBLE
2. TUNGSTEN CRUCIBLE
3. FLAT TUNGSTEN HEATING ELEMENT (4)
4. TANTALUM RADIATION SHIELDS
5. SIDE COPPER COOLING COILS
6. TOP WATER COOLED ELECTRODE SUPPORT CONDUCTOR
7. REFLECTION SHIELD INSERT
8. TO VACUUM SYSTEM
9. "O" RING GASKET SEALS
10. TOP COPPER COOLING COILS
11. TOP INTERCHANGABLE COVER FOR MEASURING APPARATUS
12. SIGHT GLASS
13. PROTECTOR MECHANISM FOR SIGHT GLASS
14. TOP TANTALUM RADIATION SHIELDS
15. COOLING WATER IN
16. COOLING WATER OUT
17. BOTTOM WATER COOLED ELECTRODE SUPPORT CONDUCTOR
18. BOTTOM PLATE FOR MOUNTING
19. WATER IN BOTTOM ELECTRODE
20. BOTTOM COPPER COOLING COILS
21. BOTTOM TANTALUM RADIATION SHIELDS
22. BOTTOM INTERCHANGABLE COVER FOR MEASURING APPARATUS
23. WATER IN TOP ELECTRODE

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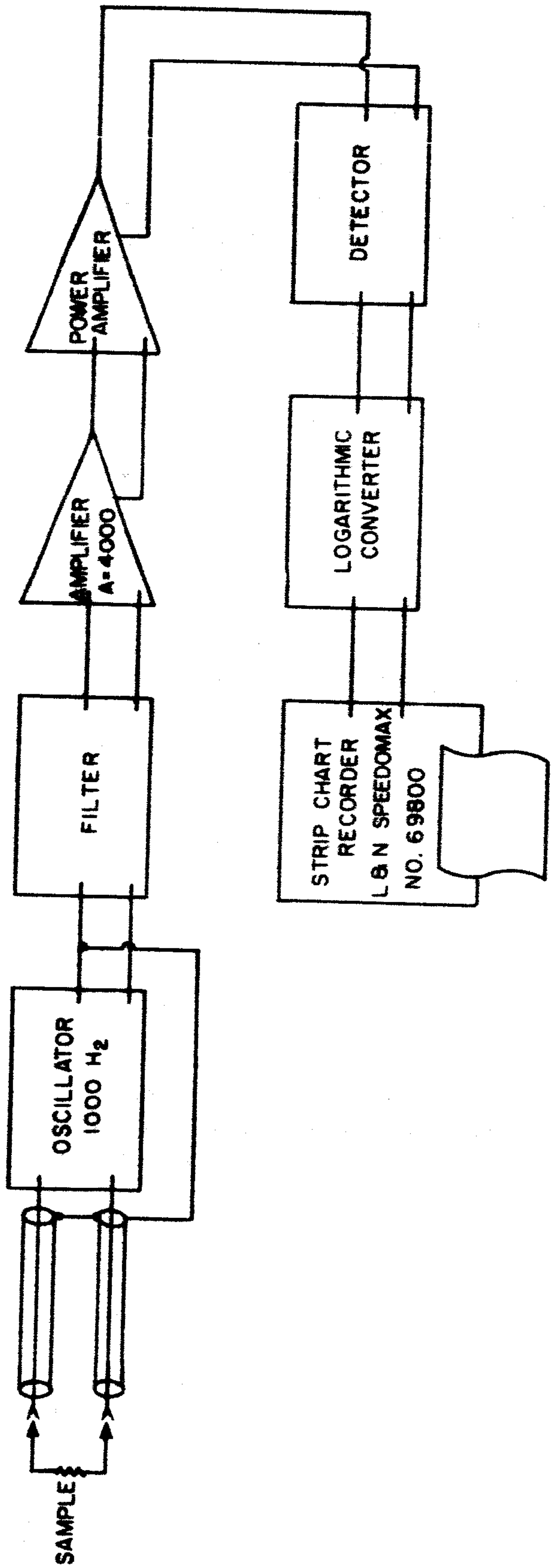
FIG. 3

LOG OHMMETER



SONIC EQUIPMENT ASSEMBLED FOR MEASUREMENT OF YOUNG'S MODULUS

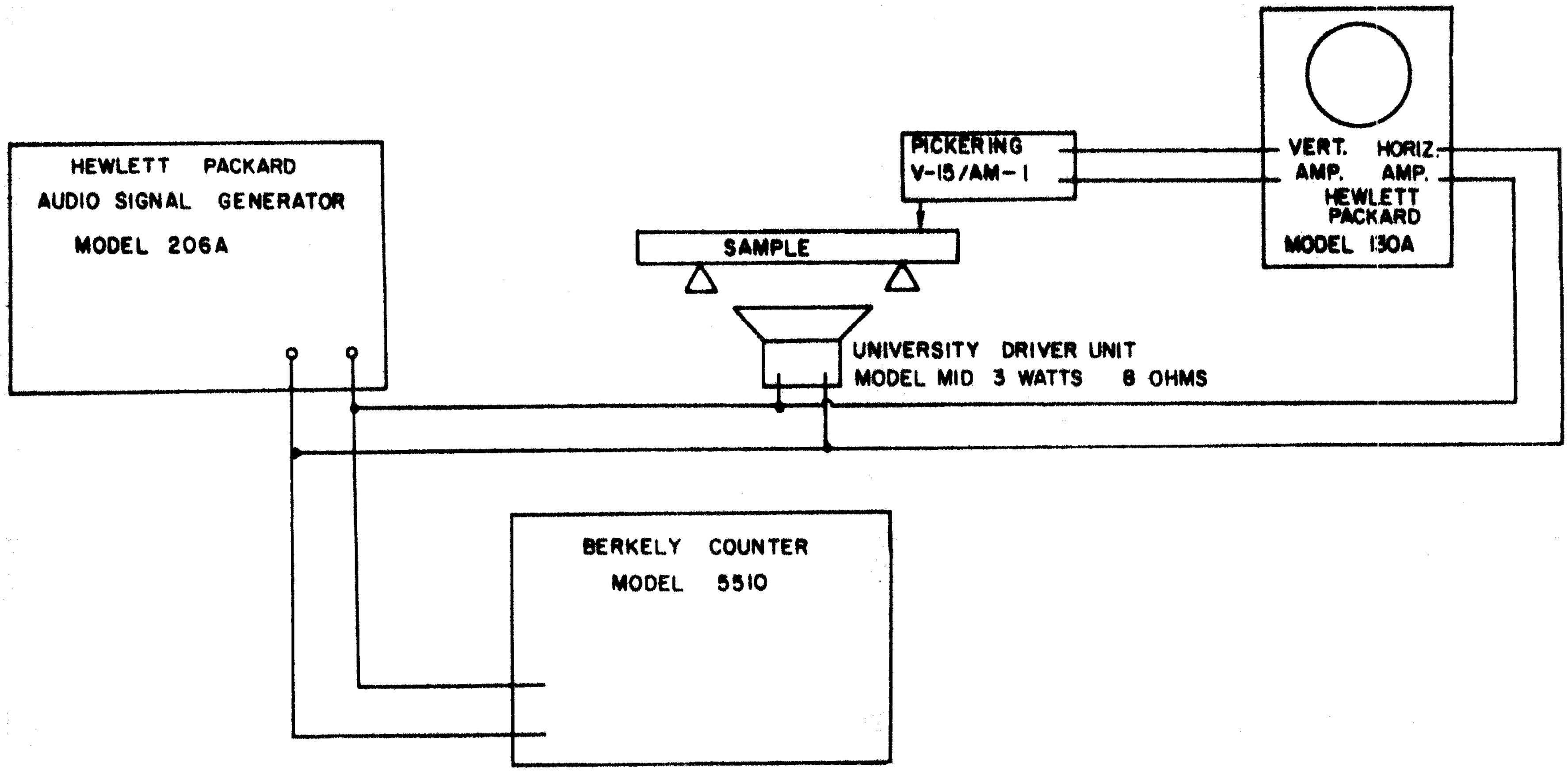


FIG. 4